TITLE: FUNDAMENTAL STUDY OF LOW-NO_X COMBUSTION FLY ASH UTILIZATION

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ABSTRACT

OBJECTIVE

This project is a collaborative effort between two universities (Brown and Princeton) and an electric utility (New England Power). The goal is to provide a more basic understanding of the nature of the organic fraction of fly ash and its role in various utilization schemes. Four specific tasks have been defined:

1. Characterization of the physical and chemical nature of ash organics. This task involves a) acquiring a suite of fly ash samples from utilities throughout the country, b) characterizing this set of samples, or a subset, with respect to organic (carbon and extractables) content, surface area and pore structure.
2. Development of new screening tests to evaluate the samples with respect to various applications. This includes further development of a test for fine carbon content and identification of a simple alternative to the foam index test, both of which can serve as measures of suitability of the ash in concrete applications.
3. Characterization of the adsorption behavior of selected fly ashes relative to various organic and inorganic adsorbates.
4. Examination of the technical suitability of high-carbon coal fly ash as a low-cost alternative to activated carbon in adsorption applications.

ACCOMPLISHMENTS TO DATE

A large ash sample bank has been assembled in this project, representing a range of ash types (class C and F) found in U.S. utility practice, encompassing various boiler types and firing configurations (tangential/wall-fired, conventional, low-NOx), coals of various rank, and selected ash samples from co-firing applications. A battery of tests is being carried out on each of these samples to characterize the chemical, physical, and adsorptive properties of the carbonaceous component. The tests include: LOI (an approximate measure of carbon content), foam index test (an industry standard measure of the strength of interaction between carbon and surfactants used in concrete mixtures), full N_2 (77 K) and CO_2 (195 K) adsorption isotherms including estimation of micropore size distributions, low-temperature oxidation reactivity, and a standard test of liquid phase adsorption properties. The work to date has shown very large variations in the specific activity (per gm carbon basis) of unburned carbon in ash toward concrete surfactants, reflecting large variations in the carbon properties.

A subset of the samples are being subjected to additional tests, including mercury porosimetry, transient adsorption experiments with liquid phase adsorbates, and polar / nonpolar surface area determination by flow microcalorimetry. During this second project period, many of the experiments performed were dictated by the importance of understanding the behavior of fly ashes in concrete systems. The key role that carbon surface area can play had been earlier identified, but did not yet provide adequate explanation as to why certain post-retrofit (low NO_X burner) ashes performed unusually poorly. Work performed this period and last period strongly suggest that the chemical nature of the carbon surface (polarity) plays an key role in surfactant interactions.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

The Nation faces a serious question concerning what to do with fly ash from coal-fired power stations. Only about 14% is presently utilized in cement and concrete products, and this is by far the largest single re-use market for this material. Most of the remainder is landfilled and thus there is clear economic incentive for utilities to seek new opportunities for utilization. This project is concerned with better characterization of the fly ash, and identification of potential new uses of the ash. It is the "organic" portion of the ash, the unburned carbon, which may be the key to success in many new utilization schemes. The unburned carbon content has been significantly increased by the introduction of new NO_x control technology and this trend may continue as NOx regulations tighten. The increased levels of carbon, and the different nature of the carbon, offer significant challenges for conventional ash utilization in concrete, but also opportunities for new markets exploiting the sorptive properties of the porous carbon residue.

PLANS FOR THE COMING YEAR

- to complete characterization of the large sample set representing the range of U.S. utility practice, and use the results to further understand the origin of poor performance in concrete.
- to test if the same trends are observed with different air entraining admixtures (i.e. concrete surfactants)
- to understand the differences between residual carbon from different ranks of coal. Low rank coals appear to give residual carbon samples that have significantly higher surface area, but lower surface-specific adsorptive activity. More work is needed to understand this.
- to continue the assessment of residual carbon as an environmental sorbent, especially in liquid-phase applications.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Journal Articles (peer reviewed)

- Freeman, E., Gao, Y.M., Hurt, R.H., Suuberg, E.S. "Interactions of Carbon-Containing Fly Ash with Commercial Air Entraining Agents for Concrete," *Fuel*, 76 (8) 761-765 (1997).

- Gao, Y.; Shim, H.; Hurt, R.H.; Suuberg, E.M.; Yang, N.Y.C. "Effects of Carbon on Air-Entrainment in Fly Ash Concrete: The Role of Soot and Carbon Black," *Energy and Fuels*, 11(2) 457-462 (1997).

Conference Presentations

- Gao, Y.; Shim, H.; Hurt, R.H.; Suuberg, E.M.; Yang, N.Y.C. "Effects of Carbon Black and fly ash carbon on Air-Entrainment in Concrete." presented at the 12th International Symposium of the American Coal Ash Association, Orlando, 1997.

- Hurt, R.; Suuberg, E., Gao, Y., Calvert, P. "Unburned Carbon in Ash: Formation, Properties, and Behavior in Construction Applications", presented at the EPRI Coal Quality Effects Conference, Kansas City, 1997.

- Kurt A. Smith, Indrek Külaots, Robert H. Hurt and Eric M. Suuberg "The Chemical Nature of Unburned Carbon Surfaces in Fly Ash - Implications for Utilization in Concrete" *1997 Ash Utilization Symposium*, University of Kentucky.

- N. Sabanegh, Y. Gao, E. Suuberg, R. Hurt, "Interaction of Coal Fly Ash with Concrete Surfactants: Diffusional Transport and Adsorption," International Coal Science Conference, 1997, Essen, Germany.

- Robert Hurt, Eric Suuberg, Yu-Ming Gao, Nader Sabanegh, Alicia Burnett, "The Undesirable Adsorption of Concrete Surfactants on Porous Carbon in Coal Combustion Fly Ash," *Carbon '97*, Pennsylvania State University, 1997.

Note: the principal investigators (Suuberg and Hurt) have organized a session at the August, 1998 American Chemical Society Meeting in Boston on the fundamental issues arising in this area. The session is entitled "Chemistry of Carbon in Fly Ash".

Students Supported under this Grant

- Indrek Külaots, graduate (Ph.D.) student in engineering, Brown University

- Nader Sabanegh, yndergraduate in chemical engineering, Brown University
  (prepared Sc.B. honors thesis on this topic)

- Kurt Smith, undergraduate in chemical engineering, Brown University
  (conducted independent study project on this topic)